Microscopic Characterization of Uranium Nitrides Synthesized by Oxidative Ammonolysis of Uranium Tetrafluoride

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The oxidative ammonolysis route was used to synthesize three uranium nitrides, \( \text{UN}_2 \), \( \text{U}_2\text{N}_3 \), and \( \text{UN} \), using \( \text{UF}_4 \) as the starting material. Powder XRD analysis showed the \( \text{UN}_2 \) and \( \text{U}_2\text{N}_3 \) products to contain less than 1.0 wt % uranium oxides. \( \text{UO}_2 \) level was identified to be 5.0 (0) wt % in the UN product as it is made, but this level increases upon exposure to air. The morphology of these nitrides was studied with SEM, while the microstructures of \( \text{UN}_2 \) and \( \text{U}_2\text{N}_3 \) were investigated by TEM techniques for the first time. An explicit microstructural characterization of UN is also presented. These characterizations showed that UN has a long-range order in its structure and bulk of the \( \text{UO}_2 \) impurities present on the UN microparticle surface, likely originating from minute oxygen impurities in the inert atmosphere cover gas and/or diffusion through the quartz reactor tube at high temperatures. Surface area measurements demonstrated a 10-fold increase in surface area during the ammonolysis step, from 0.03 to 0.26 m\(^2\)/g, and minimal change during the denitrifying step.

1. Introduction

Uranium(III) mononitride (UN) has a number of favorable nuclear fuel properties when compared to uranium oxide, including high fissile atom density, high melting point, and high thermal conductivity.\(^4\) As a result, UN is receiving attention as a potential fuel for next-generation nuclear power systems. In nuclear fuel applications, pellets of a nitride, oxide, carbide, or other actinide compounds are sintered from a powder starting material. The pronounced influence of particle size, morphology, and surface area on the nuclear fuel properties of the final sintered pellet\(^2\) provides the motivation for characterization of the starting powders.

Carbothermic reduction has been used extensively to synthesize nitride fuel material.\(^3\) In the carbothermic reduction/nitrification process, metal oxides are mixed with carbon and then annealed at 1600–1700 °C in an atmosphere of \( \text{N}_2 \) or \( \text{N}_2/\text{H}_2 \). The carbothermic process faces challenges in producing a high-density product free of oxide and carbide impurities.\(^4\)–\(^6\) For mixed actinide fuel materials, these problems are further compounded by the need to incorporate americium into the fuel matrix. Americium has a sufficiently high vapor pressure at the temperatures used during the carbothermic process\(^7\) to cause volatilization loss and contamination problems when synthesizing mixed actinide nitrides.\(^8\)

Alternate routes for the synthesis of uranium nitrides have been previously explored, including conversion of the metal hydride or metal directly to the nitride under nitrogen gas,\(^9\) ammonolysis of the metal or metal carbide to the nitride,\(^10\) and ammonolysis of the metal fluoride.\(^11,12\) Ammonolysis of the metal fluoride is particularly interesting due to the significant reductions in process temperatures required to convert the metal oxides to the nitride compared to the carbothermic reduction route. In the low-temperature fluoride oxidative ammonolysis route, \( \text{UF}_4 \) is reacted with an atmosphere of gaseous ammonia to form uranium(VI) dinitride (\( \text{UN}_2 \)).\(^11,12\) The dinitride can be reduced to uranium sesquinitride (\( \text{U}_2\text{N}_3 \)) and UN under inert atmosphere from 700 to 1100 °C.\(^13\)

Uranium nitrides have been characterized by many techniques: X-ray powder diffraction, neutron powder diffraction,\(^10,14\) vibrational spectroscopy,\(^15\) and other techniques.\(^16\) The oxidative ammonolysis route offers a significant advantage in that it provides a method to synthesize UN from the metal fluoride without involving the use of reactive gases or metal fluxing agents.\(^8\)

**References**

tion,\textsuperscript{14} nuclear magnetic resonance,\textsuperscript{15} transmission electron microscopy,\textsuperscript{16,17} and X-ray photoelectron spectroscopy.\textsuperscript{18} The compounds UN\textsubscript{2}, U\textsubscript{2}N\textsubscript{3}, and UN are the common nitrides of uranium\textsuperscript{19} and have unique crystallographic properties that can be used to differentiate one from another. The UN\textsubscript{2} compound has a CaF\textsubscript{2}-type face-centered cubic lattice with a lattice parameter of 0.531(1) nm,\textsuperscript{20} while UN is a NaCl-type face-centered cubic lattice with a cubic lattice parameter of 0.48880(1) nm when pure.\textsuperscript{21} The lattice parameter of UN is sensitive to carbon impurities\textsuperscript{22} and insensitive to small oxygen impurities.\textsuperscript{23} Both UN\textsubscript{2} and UN are indexed in the Fm\textit{3}m space group.\textsuperscript{24} The U\textsubscript{2}N\textsubscript{3} compound is body-centered cubic with a cubic lattice parameter of 1.0678(5) nm and indexed in the \textit{I}a\textit{3} space group. Uranium nitrides form a continuous phase between the dinitride and the sesquinitride. Lattice parameters and the resulting X-ray characterization.\textsuperscript{26} Uranium nitride samples prepared by observing the cross-sectional as well as microstructural morphology and microstructure of uranium nitride samples. Because microcrystalline properties influence the sinterability of UN and a fuel-quality sintered UN pellet is the ultimate goal of any nitride fabrication process for nuclear fuel, it is important to characterize the starting nitride material in sufficient detail. The quantity and consistency of oxide impurities affects the microscale and nanoscale morphology of UN, which ultimately determines the quality of the final sintered pellet\textsuperscript{17} necessitating characterization of oxide species in the nitride matrix.

In this work, the low-temperature fluoride route was used to synthesize UN\textsubscript{2}, U\textsubscript{2}N\textsubscript{3}, and UN, whose phase purity and morphology was then examined by powder XRD and SEM/TEM, respectively. This work reports for the first time the microstructures of UN\textsubscript{2} and U\textsubscript{2}N\textsubscript{3} examined by TEM. The microstructural characterization of UN is also presented and predicts the location of UO\textsubscript{2} impurity phase in the nitride matrix based on the results of the microparticles that have been investigated by TEM. The relative concentration of uranium species in the solids were determined by Rietveld analysis of the X-ray powder diffraction patterns. Surface area measurements of the fluoride and nitride species are presented as an indication of the sinterability and surface reactivity of the material and to track the microstructural changes during the ammonolysis step.

2. Experimental Details

2.1. Synthesis of Uranium Nitrides. The direct ammonolysis of UF\textsubscript{4} was used to synthesize UN\textsubscript{2}. A 1015.8 mg batch of UF\textsubscript{4} (International Bio-Analytical Industries, Inc.) was loaded in a quartz boat wrapped with platinum foil and placed inside a 25.4 mm diameter quartz tube, capped on either end with 25 mm quartz Solv-Seal fittings (Apperson Glass Co., Inc.). Pyrex Solv-Seal caps fitted with 15 mm high-vacuum Teflon stopcocks sealed the tube and allowed a controlled atmosphere to blanket the sample. The sample was held at 800 °C for 60 min under ammonia gas (research grade, Praxair), after which 858.5 mg of UN\textsubscript{2} was obtained. A 218.7 mg batch of U\textsubscript{2}N\textsubscript{3} was synthesized by heating 225.4 mg of the synthesized UN\textsubscript{2} under an inert atmosphere (ultra-high-purity argon, 99.9999%, Praxair) at 700 °C for 60 min. A separate 35.8 mg UN\textsubscript{2} sample was heated to 1100 °C for 30 min under an inert atmosphere producing 34.0 mg of UN.

2.2. Characterization Methods. 2.2.1. XRD. X-ray powder diffraction (XRD) patterns were obtained at the department of Geoscience of University of Nevada, Las Vegas using a Philips PANalytical X’Pert Pro instrument with a Cu K\textalpha target and a Ni filter, using 40 mA current and 40 kV tension. Phase composition was determined using the following reference patterns from the International Center for Diffraction Data: UN\textsubscript{2} (01-073-1713), U\textsubscript{2}N\textsubscript{3} (01-073-1712), UN (00-032-1397), and UO\textsubscript{2} (00-041-1422). A lanthanum hexaboride internal standard (SRM 660a) was adixed with the uranium nitride samples before acquisition of the XRD powder patterns in order to perform Rietveld analysis\textsuperscript{27} on the experimental XRD patterns to determine cubic lattice parameters and X-ray densities of each nitride sample. Instrumental parameters were optimized with the XRD pattern obtained for the internal standard by utilizing the reference ICDD pattern number 00-034-0427.

2.2.2. Surface Area Analysis. Surface area analysis (SAA) was performed on a Quantachrome Nova 1000, which uses the Brunauer–Emmett–Teller method.\textsuperscript{28} Nitrogen is used as the adsorbing gas at a working pressure below 100 kPa. No reactions with any compounds occurred during the experiment within the SAA working temperature range of 77–310 K. To avoid potential thermal decomposition or oxidation, samples were degassed at ambient laboratory temperature of 298–310 K.

2.2.3. Microscopy. The morphology of the nitride samples was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM imaging was performed on a JEOL scanning electron microscope model JSM-5610 equipped with secondary electron (SE) and backscattered electron (BE) detectors and an Oxford ISIS EDS (energy-dispersive spectrometer)

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\textsuperscript{24} Tagawa, H. \textit{J. Nucl. Mater.} 1974, 51, 78.
\textsuperscript{26} Silva, G. W. C.; Ma, L.; Hemmers, O.; Lindle, D. \textit{Micron} 2008, 39, 269.
system with an acceleration voltage of 15 kV. Gold-coated powder samples mounted on double-sided carbon tapes were used to investigate the bulk particle morphology of the samples using the SE imaging mode of SEM. A JEOL electron probe microanalyzer model JXA-8900 equipped with four wavelength-dispersive X-ray spectrometers and an EDS was used to quantitatively analyze the elemental distributions in the samples.

A Tecnai-G2-F30 supertwin transmission electron microscope system with a 300 keV Schottky field emission gun was used to characterize the samples. Bulk morphology was analyzed using the conventional bright field (BF) mode, and lattice structure was analyzed using the high-resolution TEM (HRTEM) mode. All TEM images were recorded using a slow scan CCD camera attached to a Gatan GIF 2000 energy filter. Web-based kinematical electron diffraction and HRTEM simulations29 were used in analyzing and confirming the HRTEM imaging of the samples. The elemental distribution of each sample was also determined using the corresponding X-ray energy-dispersive spectrometry (XEDS) under the STEM mode (scanning transmission electron microscopy) condition.

2.3. TEM Specimen Preparation. Two techniques were used for TEM specimen preparation: solution-drop and microtome cutting. The solution-drop method was utilized to explore the morphology of the nitrides samples. Microtome cutting was used to prepare samples for cross-section analysis and HRTEM imaging.

To prepare samples by the solution-drop method, 1–5 mg of the sample material was ground by hand in a mortar and pestle and added to 5.0 mL of reagent-grade methanol. This mixture was agitated in an ultrasonic water bath for 5 min to form a homogeneous colloidal suspension. One drop of the suspension was placed onto a 3 mm diameter carbon-coated copper grid using a small-tipped transfer pipet. The solution was evaporated from the sample at room temperature, leaving the fine particulate sample deposited on the carbon film, which was then used in the TEM observation.

For the microtome cutting method, several milligrams of sample were mixed with spur resin26 in a microvial, which was then solidified by drying at 60 °C overnight. The spur resin used for these samples was a mixture of 10.0 g of ERL (vinylecyclohexene dioxide), 4.0 g of DER (diglycidyl ether of polypropylene glycol), 26.0 g of NSA (nonenyl succinic anhydride), and 0.4 g of DMAE (dimethylaminoethanol). The sample embedded in the resin was cut into slices with a thickness of 20–50 nm using a Leica EM UC6rt microtome. The resulting samples were loaded onto a 3 mm copper grid for TEM analysis.

3. Results

3.1. Chemical Analysis Using XRD and Electron Microprobe. Powder XRD patterns of the UN2, U2N3, and UN samples are shown in Figure 1, and the narrow, well-defined, high-intensity peaks indicate these samples are decidedly crystalline.30 On the basis of the Rietveld analysis applied to the XRD patterns, the as-synthesized UN2 sample consisted of a 0.6 (3) wt % secondary oxide phase. There are also peaks in the UN2 spectrum at 20.2° and 36.1° 2theta values (Figure 1a) that have some resemblance to the peaks identified in the U2N3 XRD pattern (Figure 1b) but are not accounted for by the UN2 structure. In order to investigate these peaks further, another UN2 sample was synthesized under the same NH3 atmosphere and temperature (800 °C) for 390 min. The Rietveld analyses of the sample held at this temperature for 60 min and the sample held for 390 min are shown in Figure 2a and 2b, respectively. The peaks at 20.2° and 36.1° 2theta values have disappeared for the sample made after heating for 390 min. Incomplete conversion, with the material still slightly substoichiometric UN2, could account for these peaks since UN2 and U2N3 are known to have a wide range of continuous stoichiometry24,25 and supersymmetries that cause weak reflections to appear in the XRD pattern. The UN sample was determined to consist of two chemical phases, the primary UN phase and a 5.0 (1) wt % UO2 impurity phase. Table 1 shows the cubic lattice parameters determined using Rietveld refinement and X-ray densities of each nitride calculated from the experimental XRD patterns, along with published values of each nitride.

Microsc. Microanal. 2004, 10 (Suppl 2); URL: http://emaps.mrl.uiuc.edu/.


Figure 1. Experimental XRD patterns of the synthesized uranium nitrides: (a) UN2, (b) U2N3, and (c) UN.

![XRD Patterns](http://emaps.mrl.uiuc.edu/)
The variable stoichiometry of the $\text{UN}_1.5 \equiv \text{x} \cdot \text{U}_2\text{N}_3$ phase likely leads to the departure from the pure compound lattice parameter and density for synthesized $\text{U}_2\text{N}_3$ and $\text{UN}_2$. Electron microprobe determination showed that there are considerable amounts of oxygen impurities in $\text{U}_2\text{N}_3$ and $\text{UN}_2$. The oxygen level is highest in $\text{UN}$ and lowest in $\text{UN}_2$. The error in the oxygen quantity measurement for $\text{UN}_2$ sample is large because the oxygen level is near the lower detectable limit of this technique.

### 3.2. Surface Area Analysis

Surface area analysis showed a 10-fold increase upon ammonolysis of $\text{UF}_4$ to $\text{UN}_2$. The surface area of the starting $\text{UF}_4$ sample was well below the specified reliable detection limit of the instrument, but the measurement was found to be repeatable with sufficient sample. Measured surface areas of the starting material and all nitrides formed are shown in Table 3.

### 3.3. Microscopy of $\text{UN}_2$

The SE-SEM image of the $\text{UN}_2$ sample (Figure 3) shows the $\text{UN}_2$ particles are primarily irregular grains with some discrete flat faces. The observed particle characteristic length distribution ranges from 0.1 to

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**Table 1. Lattice Parameters and X-ray Phase Densities of the Uranium Nitrides Calculated from Experimental Patterns Using Rietveld Analysis**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{a}$ (nm)</th>
<th>$\bar{a}$ (nm)</th>
<th>$\bar{a}$ (nm)</th>
<th>$\bar{a}$ (nm)</th>
<th>$\bar{a}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{UN}_2$</td>
<td>0.53027(1)</td>
<td>0.5316(1)</td>
<td>0.5316(1)</td>
<td>11.8516(2)</td>
<td>11.7300(2)</td>
</tr>
<tr>
<td>$\text{U}_2\text{N}_3$</td>
<td>1.06691(1)</td>
<td>1.0678(1)</td>
<td>1.0580(5)</td>
<td>11.3430(2)</td>
<td>11.2400(2)</td>
</tr>
<tr>
<td>$\text{UN}$</td>
<td>0.48899(1)</td>
<td>0.48899(2)</td>
<td>0.48999(3)</td>
<td>14.3175(5)</td>
<td>14.3200(2)</td>
</tr>
</tbody>
</table>

**Table 2. Elemental Compositions Determined by Electron Microprobe Studies**

<table>
<thead>
<tr>
<th>Sample</th>
<th>U  (at%)</th>
<th>N  (at%)</th>
<th>O  (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{UN}_2$</td>
<td>89.02 ± 1.72</td>
<td>10.68 ± 0.20</td>
<td>0.29 ± 0.38</td>
</tr>
<tr>
<td>$\text{U}_2\text{N}_3$</td>
<td>90.77 ± 1.64</td>
<td>8.26 ± 0.10</td>
<td>0.97 ± 0.30</td>
</tr>
<tr>
<td>$\text{UN}$</td>
<td>93.17 ± 1.94</td>
<td>5.14 ± 0.13</td>
<td>1.69 ± 0.41</td>
</tr>
</tbody>
</table>

**Table 3. Measured Surface Areas**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{UF}_4$</td>
<td>0.03 (3)</td>
</tr>
<tr>
<td>$\text{UN}_2$</td>
<td>0.26 (3)</td>
</tr>
<tr>
<td>$\text{U}_2\text{N}_3$</td>
<td>0.26 (3)</td>
</tr>
<tr>
<td>$\text{UN}$</td>
<td>0.23 (3)</td>
</tr>
</tbody>
</table>

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6 µm, with incompletely crystallized particle faces making it difficult to measure the particle sizes accurately.

The TEM image of the UN$_2$ specimen prepared using the solution-drop method (Figure 4a) shows several agglomerated particles. Because they reside as aggregates, it is difficult to identify any particular shape of the UN$_2$ particles using this sample preparation technique. The characteristic lengths of the particles in the TEM images (150–450 nm) are in the lower range of the length distribution identified in the SEM imaging (100–6000 nm) because of the higher magnification attainable with TEM imaging. A higher magnification TEM BF image of the edge of the particle (Figure 4b) shows no detectable precipitates, defects, or faceted surfaces, indicating that the focus area of the particle does not have detectable impurity phases.

Figure 5a is the cross-sectional TEM BF image of another UN$_2$ particle, used to obtain the SAD pattern in Figure 5b. Most of the major electron diffraction spots in this SAD pattern correspond to the diffraction of UN$_2$ in the {111} direction in reciprocal space under [011] zone axis. Most of the other diffraction spots due to UN$_2$ are not indexed for reasons of figure clarity. The diffraction spots circled could be due to minor secondary phases such as UO$_2$, and the weak diffractions in the background of the SAD pattern are probably due to polycrystallinity within the focused particle area. The lattice fringes in the HRTEM image in Figure 5c correspond to the interplanar d spacing of UN$_2$ unit cell in (111) projection (for UN$_2$, $d_{111} = 0.30657 \text{ nm}$).

3.4. Microscopy of U$_2$N$_3$. The SE-SEM image of U$_2$N$_3$ sample particles (Figure 6) shows a similar morphology to that of the UN$_2$ sample: irregular grains with incompletely crystallized faces. The particle sizes range from 0.1 to 6 µm, also similar to the UN$_2$ sample.

The TEM BF image of a microtome cut U$_2$N$_3$ sample is shown in Figure 7a. The black spots in this image are due to mass contrast contributed by multiple overlapping U$_2$N$_3$
particle layers. Because of these layers, most of the region in the bulk of the TEM BF image is too dense to see a clear picture of $U_2N_3$ morphology. However, the thickness decreases at the edge of the sample, which allows for quality imaging. No secondary phase precipitates or defects in $U_2N_3$ are visible in these thin edge areas. The SAD pattern shown in Figure 7b shows the zone axis is along [111]. The weak diffraction spots, as well as some stronger spots possibly corresponding to double diffractions (circled in the image), are due to minor secondary phases ($UO_2$) and grain overlapping. Grain boundaries can also be observed in the HRTEM image (Figure 7c), which shows lattice fringes in different orientations corresponding to (220) and (422) diffracting planes.

3.5. Microscopy of UN. Particles in the UN sample (Figure 8) appear to have the same size distribution as the $UN_2$ and $U_2N_3$ samples. However, the UN particle faces appear noticeably less sharp. While the higher nitride samples show a majority of the larger particles having discrete sharp faces, very few of the similarly sized UN particles have observable flat sharp faces. This observation suggests that either the image is out of focus a little or the UN sample is less crystalline than the higher nitride precursor species.

The TEM BF micrograph in Figure 9a shows several UN particles prepared for imaging by the solution-drop method. Magnified TEM BF images focused on two thin edges, B and C, of one UN particle are shown in Figure 9b and 9c, respectively. The particles shown in this image range from 100 to 150 nm in length, which is in the lower end of the particle size distribution observed in the SEM image. The lack of contrast in the bright field image caused by the high electron scattering factor of UN tends to suppress the detailed structure information, making it difficult to detect the presence of any secondary phases in the BF mode image shown in Figure 9a. However, the magnified images of the selected particles in Figure 9b and 9c show no indication of morphological changes corresponding to a secondary phase. The same two particles in Figure 9b and 9c were used to obtain the HRTEM images shown in Figures 10 and 11, respectively.

The HRTEM image, which was obtained focusing the edge of the particle in Figure 9b, of UN in Figure 10 shows a number of grain boundaries between UN and $UO_2$ phases. UN was identified in the bulk part of the particle, while the lattice fringes near the edge of the particle correspond to the $UO_2$ phase. The $UO_2$ phase intrudes 10–20 nm from the edge of the particle into the interior. Most of the particle edge contains details of the $UO_2$ chemical phase in only one of the [111] directions, and in some patches (area A in Figure 10) the details of the structure is absent. Only one area (area B in Figure 10) contains the fringe details in both directions.

The HRTEM image shown in Figure 11 was obtained by focusing on a thin area of the middle of the particle in Figure 9c highlighted with a box. This image shows no indication of the presence of $UO_2$ as a secondary phase in this area, supporting the hypothesis that the oxide present in the sample is due to environmental oxidation at the particle surface rather than $UO_2$ inclusions nucleated within the bulk of the UN phase. The lattice fringes in the image are parallel to the (111) planes of UN structure. Furthermore, the lattice fringes...
show a long-range order with different multiplicities of tunnel rows. There are three different tunnel rows: 2-, 3-, and 4-fold. The experimental intensity profiles shown in Figure 11c, 11d, and 11e were obtained along the lattice fringes normal to line segments AB, CD, and EF, respectively. These profiles confirm the tunnel multiplicities (2-, 3-, and 4-fold) of the long-range order in the lattice fringes. The FFT micrograph (Figure 11b) also indicates the presence of well-resolved lattice fringes.

Cross-sectional TEM images of a UN particle that was microtome-cut to a thickness of 25 nm are shown in Figure 12. The particle shown in Figure 12a indicates the presence of some Moiré fringes at the surface of the particle, most likely due to the overlapped crystallographic planes of UN with the UO$_2$ impurity phase. The HRTEM image in Figure 12b was obtained by focusing on the particle area as indicated in Figure 12a. There are a number of grains with lattice fringes in different orientations, confirmed by the FFT micrograph (Figure 12b inset). These regions of different lattice fringe orientation are denoted by letters A–F. Lattice fringes in region A show structure details in all directions of [011] reflections. In all other locations, only one lattice fringe direction can be seen due to the specific grain orientation relative to the microtome-cut surface being imaged. The poorly formed larger-scale fringes observed between locations A and B are likely due to a tilt boundary being imaged roughly parallel to the subgrains. Again, the UO$_2$ phase can be identified by the 0.335 nm lattice fringe spacing at the edge of the grain.

Figure 13 shows a magnified HRTEM image of region A in Figure 12b. Lattice fringes are parallel to the (200) planes of UN. The calculated HRTEM image (Figure 13b) of UN in the (200) projection with the [011] beam direction using 25 nm thickness and 65 nm defocus value confirms the lattice fringe orientation in the image. Also, considering the orientation of the unit cell determined by the FFT micrograph and a unit cell model (Figure 13c) an approximate value of 0.483(10) nm can be determined for the lattice parameter of UN.

4. Discussion

The XRD patterns of samples produced by the oxidative ammonolysis process showed the UN$_2$ and U$_2$N$_3$ products have high phase purity, with possible contaminations of UN$_{2-X}$ incompletely crystallized impurities plus a minimal secondary UO$_2$ phase due to synthesis equipment or atmosphere. Although the SAD patterns indicated the presence of impurity phases in minimal quantities, impurity levels were below those observable by either TEM BF or HRTEM imaging. It was also found that some of the peaks in the UN$_2$ XRD pattern can be reduced by heating for longer time periods under NH$_3$ atmosphere. However, the longer heating time increased the oxide contamination levels, which in turn
would affect the phase purity of the final UN sample using the described synthesis equipment. On the basis of the results obtained through this work, production of high-purity UN does not appear to require reacting the fluoride starting material past the point at which it is fully converted to a uranium nitride, even though the intermediate UN₂ product may be slightly hyperstoichiometric.

HRTEM analysis of the UN samples confirmed that the bulk of the particle consist of UN, as suggested from the XRD pattern, with a UO₂ secondary phase forming on the surface of particles observed (Figures 10 and 12b). The large interior region of the UN lattice fringes, corresponding to the (200) plane (Figure 10), is uninterrupted by UO₂ inclusions. This supports the conclusion that oxide impurities are likely to be formed by a diffusive process from the synthetic environment and thus are also likely to form along the particle surface. Given the high reactivity of UN in any environment not completely devoid of oxygen, contamination from the experimental apparatus is likely to be the source of these oxide impurities rather than the synthetic route. Subsequent analysis of the UN sample after it had been allowed to age for 3 months shows the ingrowth of oxide contamination, lending support to this initial hypothesis. The quantitative analysis performed on the XRD patterns of both these samples showed that the UO₂ level increases from 5.0 (1) to 14.8 (1) wt % over this time period (Figure 14).

Further determination of oxygen impurity levels on the surface of these three samples was done using the XEDS in the STEM mode of TEM. Figure 15 shows the elemental distributions of UN₂, U₂N₃, and UN results determined using XEDS. Uranium and nitrogen are visible in all three samples, but the presence of oxygen in a considerable amount was detected only in the UN sample. Thus, XEDS confirms that the oxide level in the bulk particle area of the analyzed particles is greatest in the UN sample, as found by XRD and electron microprobe.

The stoichiometry between uranium and nitrogen in uranium nitrides is known to be a continuous variable from UN₁.₇₅ to UN₂₂ for UN₂ and UN₁.₄₅ to UN₁.₇₅ for U₂N₃.²⁴,²⁵ However, for the lower nitrides the stoichiometry range is smaller, UN₀.₉₉₅–UN₀.₉₉₉, than that of the higher nitrides. The refined lattice parameters of UN₂- and U₂N₃-synthesized samples show a match to the reference values only up to the second decimal point (Table 1). The X-ray densities of these two nitrides also vary accordingly. However, the lattice parameter and X-ray density of the synthesized UN matches

![Figure 14. XRD/Rietveld analysis comparison of the UN powder sample: (a) as-synthesized UN, (b) UN sample after 3 months.](image-url)
with the reference value within the confidence intervals reported. Thus, the lattice parameter variance in the higher uranium nitrides (UN$_2$ and U$_2$N$_3$) likely indicates the vast range of stoichiometry identified by other authors. The absence of variance in the lattice parameter for the synthesized UN confirms its phase purity to expectations given the narrow range of stoichiometry reported for UN.

As-synthesized uranium mononitride particles appeared to fall within a particle size distribution of 0.1–6 µm. Furthermore, the particle sizes estimated by SEM were verified by TEM. This particle size range is consistent with the previously reported microscopic data, and it is similar to the

5. Conclusion

Uranium nitrides synthesized using the oxidative ammonolysis of UF$_4$ were successfully characterized by means of XRD, electron microscopy, and surface area analysis. For the first time, TEM BF and HRTEM techniques were applied in morphological and microstructural observations of UN$_2$ and U$_2$N$_3$. The UN samples synthesized from UN$_2$ contained measurable levels of UO$_2$, as high as 5.0 (1) wt %.

The TEM observations of this UN sample showed that UN has long-range order in its microstructure. Furthermore, the HRTEM images of microparticle surface and cross-section made by solution-drop and microtome-cutting methods, respectively, showed the secondary oxide phase formed primarily on the UN particle surface. Given the absence of an oxide phase in the UN$_2$ and U$_2$N$_3$ samples in large quantities, oxide contamination appears to form during the final stage of the process, most likely due to oxygen contamination in the experimental system used for this synthesis. Observed increases in uranium oxide levels in UN after long-term exposure to air support the conclusion.

Better oxygen control during the final decomposition reaction, such as replacement of the quartz furnace tube and addition of oxygen getters for the cover gas, may be sufficient to reduce the oxide levels within the UN product as well as storage of the UN samples under inert atmosphere. This would allow for production of sintered UN pellets and testing of the sinterability of UN from this synthetic route.

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